

Structure and Stability of B_{13}^+ Clusters

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Received 8 July 1997; accepted 15 August 1997

ABSTRACT: The structures and energies of B_{13}^+ , observed experimentally to be an unusually abundant species among cationic boron clusters, have been studied systematically with B3LYP/6–31G* density functional theory. The most thermodynamically stable B_{12}^+ and B_{13}^+ clusters are confirmed to have planar or quasipolar rather than globular structures. However, the computed dissociation energies of the 3-dimensional B_{13}^+ clusters are much closer to the experimental values than those of the planar or quasipolar structures. Hence, planar and 3-dimensional B_{13}^+ may both exist. © 1998 John Wiley & Sons, Inc. *J Comput Chem* **19**: 203–214, 1998

Keywords: structure; stability; B_{13}^+ clusters; B3LYP/6–31G* density functional theory

Introduction

On 1987 Hanley et al.^{1a,b} used mass spectrometry to detect the existence of the cationic boron clusters (B_n^+) produced by laser ablation of isotopically pure solid boron followed by collision-induced dissociation with Xe. Peaks corresponding to $n = 5, 10, 11$, and 13 always exhibited anomalously high intensity. In addition, collision experiments of B_n^+ with small molecules (O_2 , D_2 , H_2O , CO_2 , N_2O) confirmed that B_{13}^+ is especially

stable.^{1c–g} Roland et al.'s² study of photoionization and photofragmentation of B_xN_y clusters produced by laser vaporization of boron nitride also yielded B_{13}^+ in high abundance among B_n^+ products when higher photoionization fluence was used.

What is the structure of B_{13}^+ ? The icosahedral $B_{12}H_{12}^{2-}$ is the most stable homologue in the *closo*- $B_nH_n^{2-}$ family, whereas $B_{13}H_{13}^{2-}$ is still hypothetical.³ Also, on the basis of the α - and β -rhombohedral B_{12} moieties in elemental boron,⁴ Hanley et al. speculated that B_{13}^+ might have an icosahedral structure (1, Fig. 1) with one encapsulated boron atom in the cluster center. The anomalous stability

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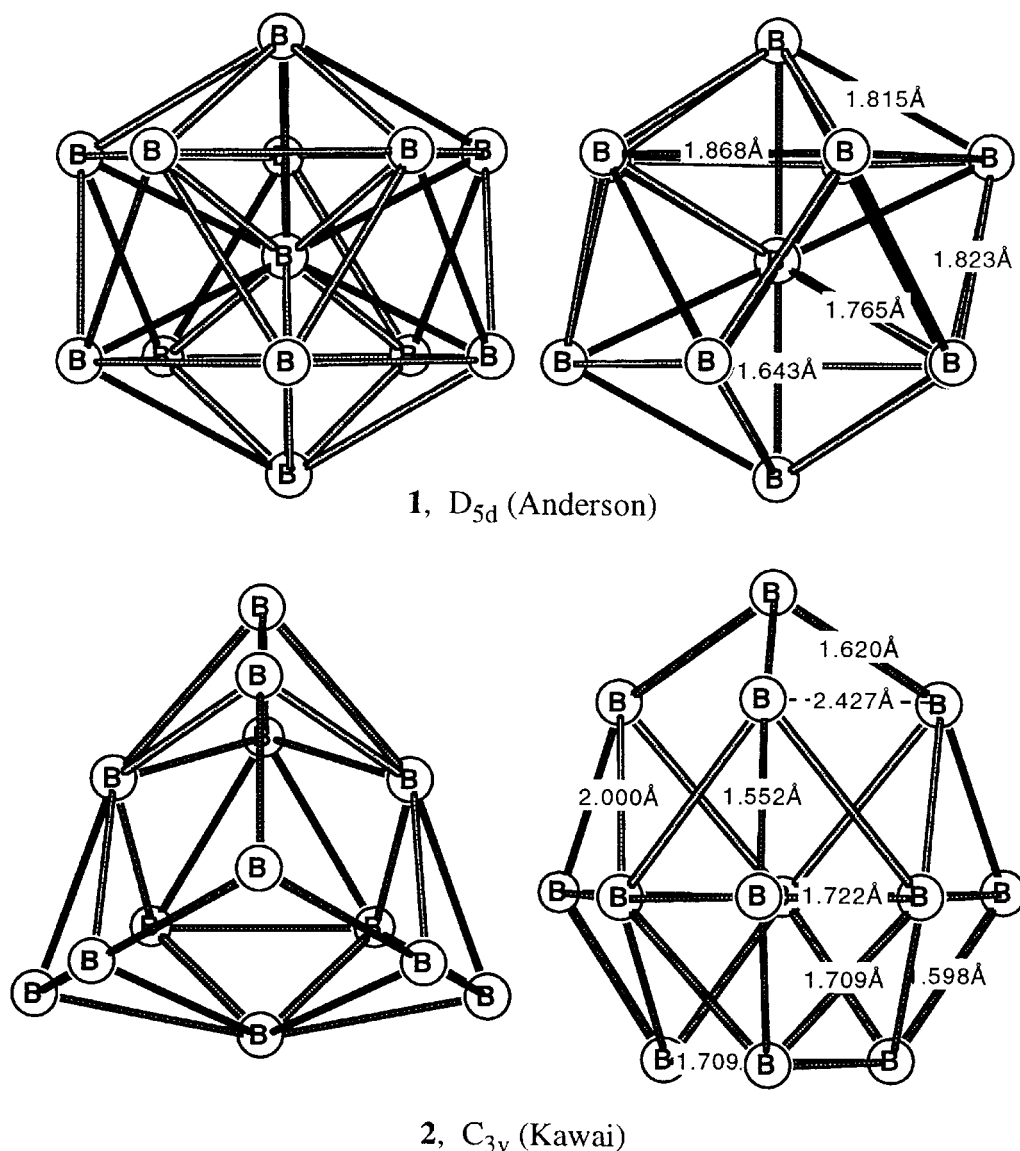


FIGURE 1. Optimized structures of B_{13}^+ clusters at the B3LYP/6-31G* level.

of B_{13}^+ was ascribed to the large number of bonding contacts in such a high coordination structure.^{1b} Is this what makes the 13-boron system B_{13}^+ so special?

Because no detailed information is given by the gas phase experiments, possible structures have been explored computationally. Kawai and Weare's⁵ Car-Parrinello *ab initio* molecular dynamics (MD) simulation found that Anderson et al.'s^{1b} icosahedral B_{13} (the framework is similar to **1**) is not even a local minimum; the encapsulated boron atom moves spontaneously out of the cage. This results in a more stable $C_{3v}B_{13}$ (similar to **2**)⁶

with a capped three-membered ring face. The large energy difference (2 eV) between the highest occupied molecular orbital (HOMO) and HOMO-1 of the $C_{3v}B_{13}$ (**2**) suggests that removal of the HOMO electron in the same symmetry will result in a particularly stable closed shell B_{13}^+ cluster with large HOMO-lowest unoccupied MO (LUMO) energy separation.

At the MP4SDTQ/3-21G//HF/3-21G level, Kato et al.⁷ first discovered the surprising result that planar structures of neutral (B_{12} and B_{13}) and cationic (B_{12}^+ and B_{13}^+) clusters are more stable than all the 3-dimensional structures tested. For exam-

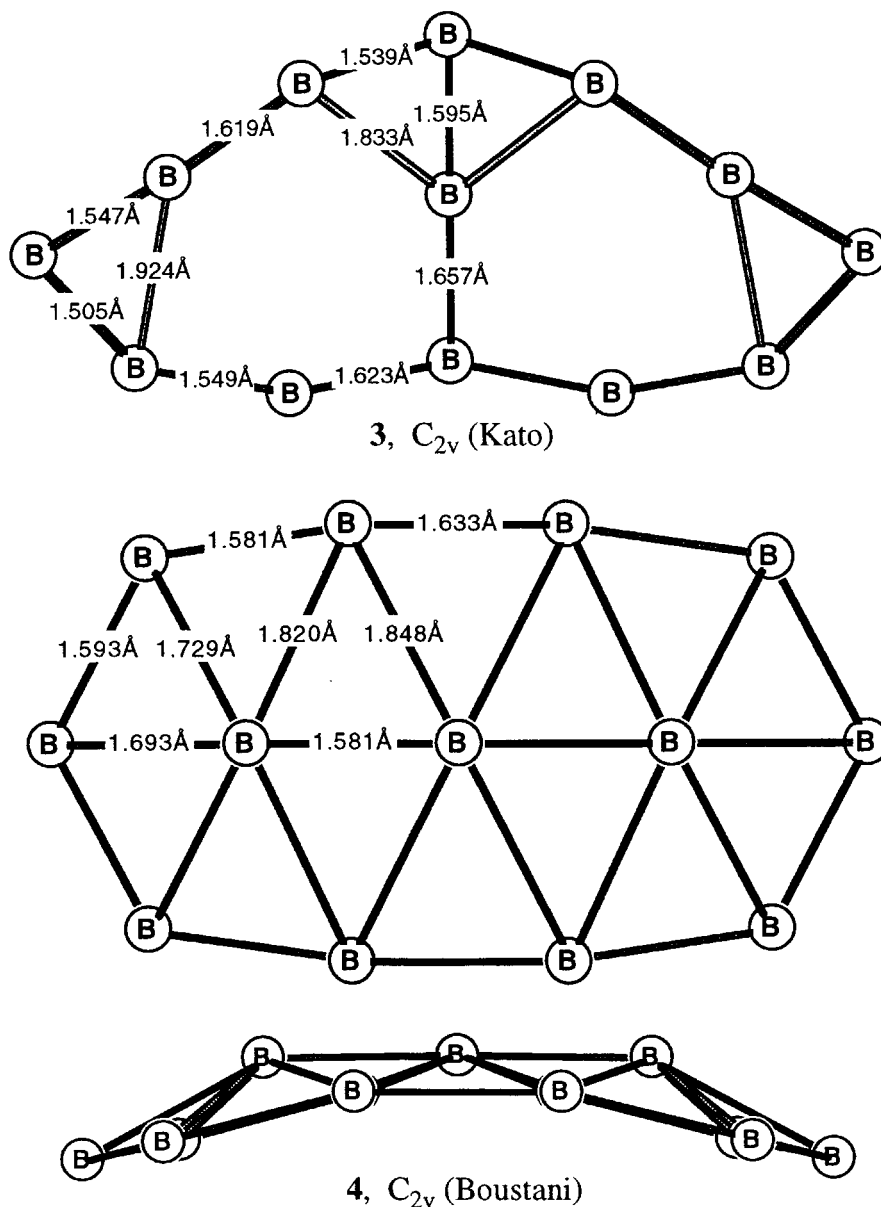


FIGURE 1. (Continued)

ple, Anderson et al.'s^{1b} proposed D_{5d} structure (1) of B_{13}^+ is only a high order saddle point at HF/3-21G (and has 12 imaginary frequencies!). The planar B_{13}^+ structure (3) is much lower in energy. However, the calculated dissociation energies of 3 for the two alternative processes [2.7 eV for eq. (1) and 2.2 eV for eq. (2)] are far from the experimental values (7.8 ± 0.9 and 8.0 ± 1.5 eV, respectively).



In a systematic density functional theory (DFT) investigation of the neutral and cationic boron clusters (B_n , $n = 2-14$) using the local spin density (LSD) approximation and nonlocal spin density (NSD) energy correction, Boustani⁸ also found that planar or quasipolar structures for the neutral and cationic boron clusters are both more stable than their 3-dimensional isomers. He favored a quasipolar structure (4) for B_{13}^+ with three hexagonal pyramids adjacent to one another in a longitudinal arrangement. However, the calculated dissociation energies (ca 5.8 eV), although improved

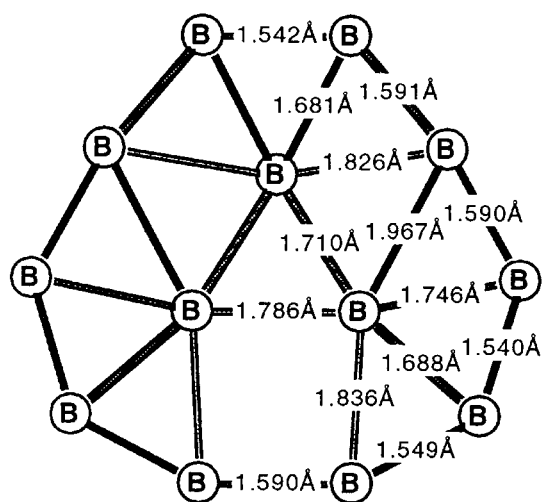
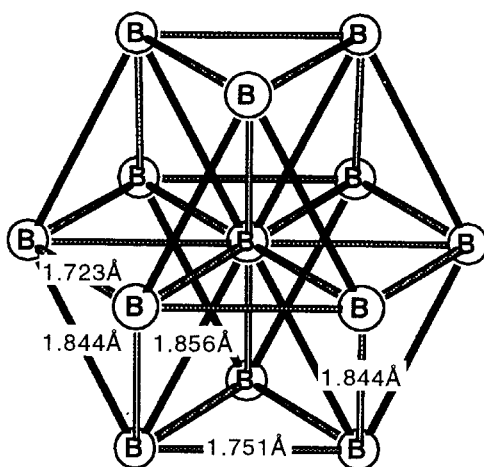
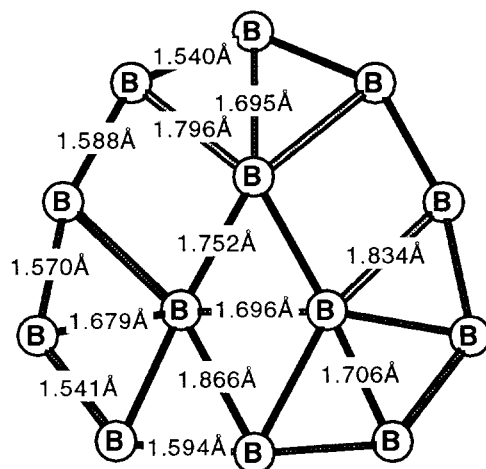
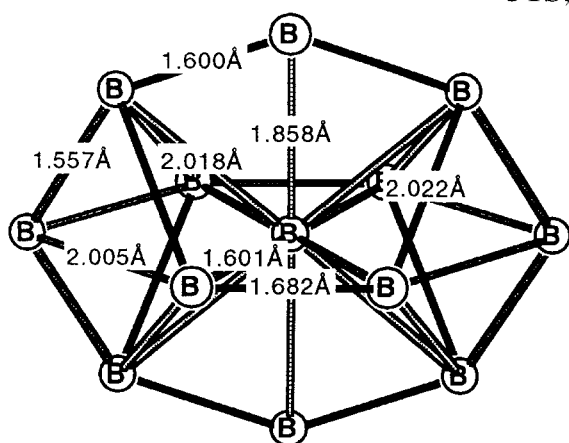
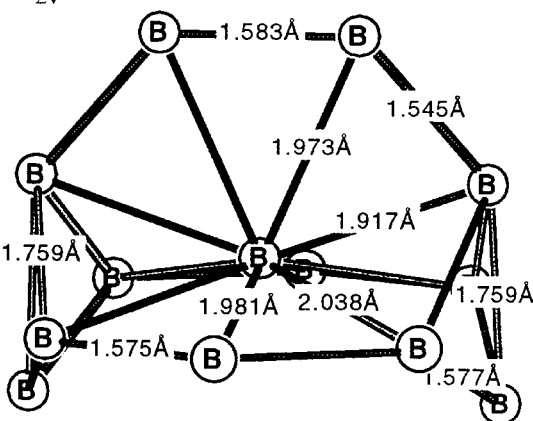
5, C_{2v} (Ricca)6, D_{3d} 5TS, C_{2v} 7, D_{2h} 8, C_{2v}

FIGURE 1. (Continued)

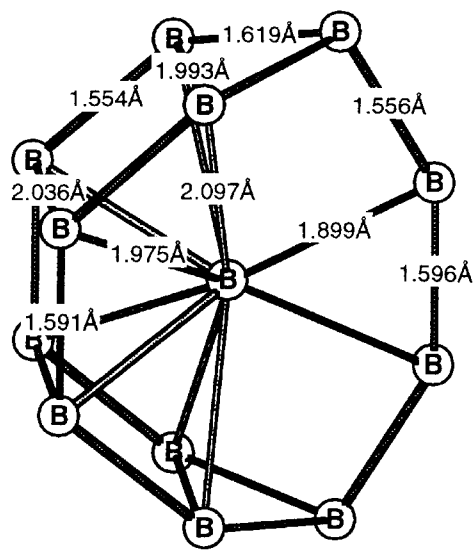
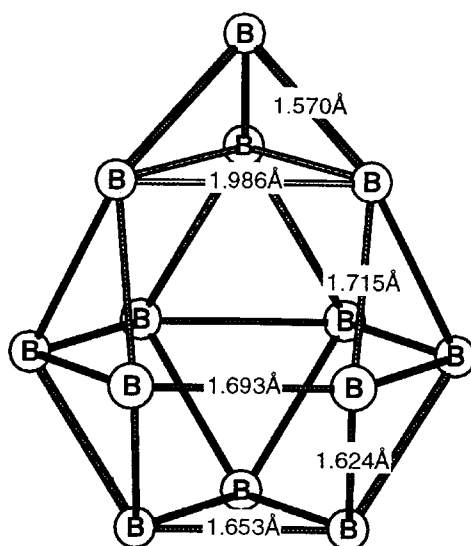
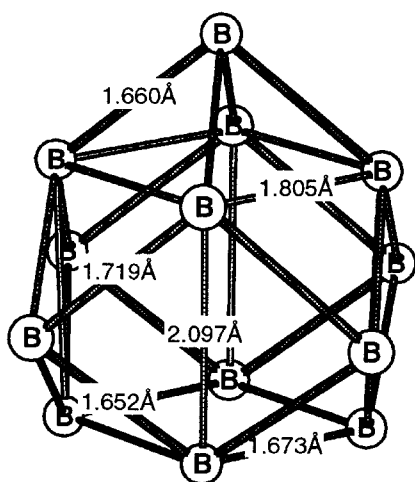
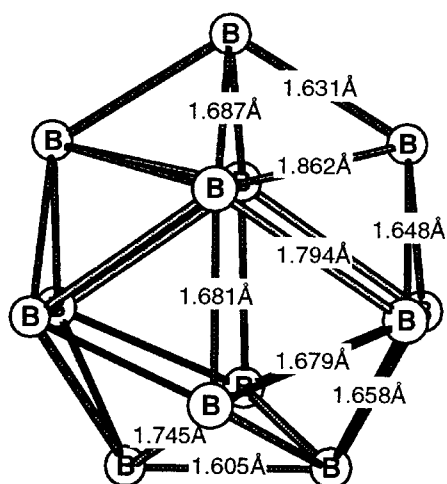
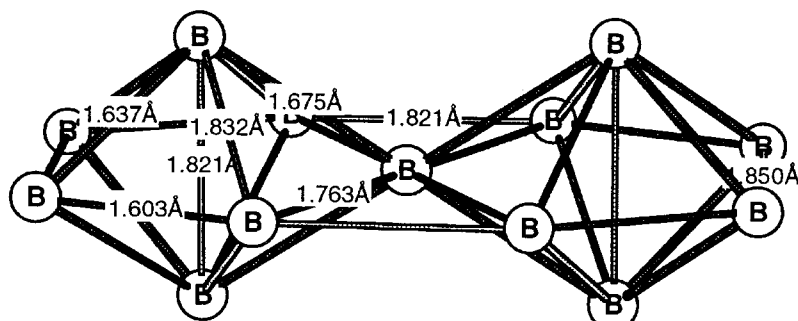
9, C_{2v} 10, C_{3v} 11, C_{4v} 12, C_{2v} 13, D_{2h}

FIGURE 1. (Continued)

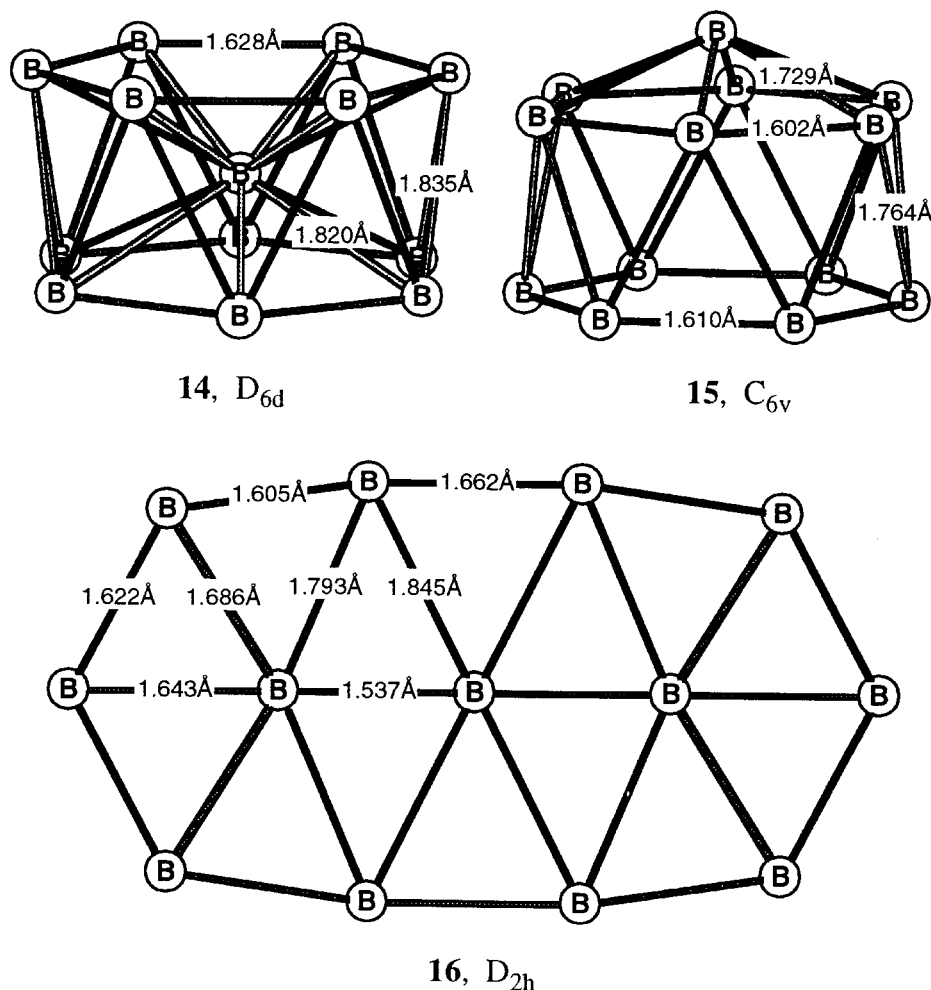


FIGURE 1. (Continued)

over Kato et al.'s *ab initio* (MP4/3-21G//HF/3-21G) values,⁷ are still well below the experimental values.

Recently Ricca and Bauschlicher⁹ reported a new planar C_{2v} structure (5) with one distorted hexagon and two distorted boron-centered heptagons. At the B3LYP/6-31G* level, this new structure is the most stable among the alternatives discussed above. However, Ricca and Bauschlicher were also unable to reproduce the experimental dissociation energy for B_{13}^+ into B and B_{12}^+ satisfactorily [5.7 eV for eq. (2)].

As pointed out by Hanley et al.,^{1a,b} the threshold for B_{13}^+ is very broad and the dissociation energies were estimated visually. Consequently, the energy of B_{13}^+ is not well established and the geometry of B_{13}^+ clusters remains unexplained. Hence, the nature of B_{13}^+ remains a challenge for computational as well as experimental chemistry.

In this study the B_{12}^+ and B_{13}^+ clusters were investigated systematically with DFT to establish the geometrical and energetic properties. We also recalculated the structures reported in the literature for comparison at the same theoretical level.

Computational Procedures

All calculations were carried out with the Gaussian 94 program.¹⁰ Geometries were fully optimized first at the *ab initio* HF/3-21G¹¹ level and then refined using DFT at B3LYP/6-31G* (i.e., with Becke's three-parameter exchange functional¹² and the nonlocal correlation potential of Lee and colleagues¹³) using the 6-31G* basis set. The calculated number of imaginary frequencies (NImag, B3LYP/6-31G*) determined the optimized structures to be minima (NImag = 0), transition struc-

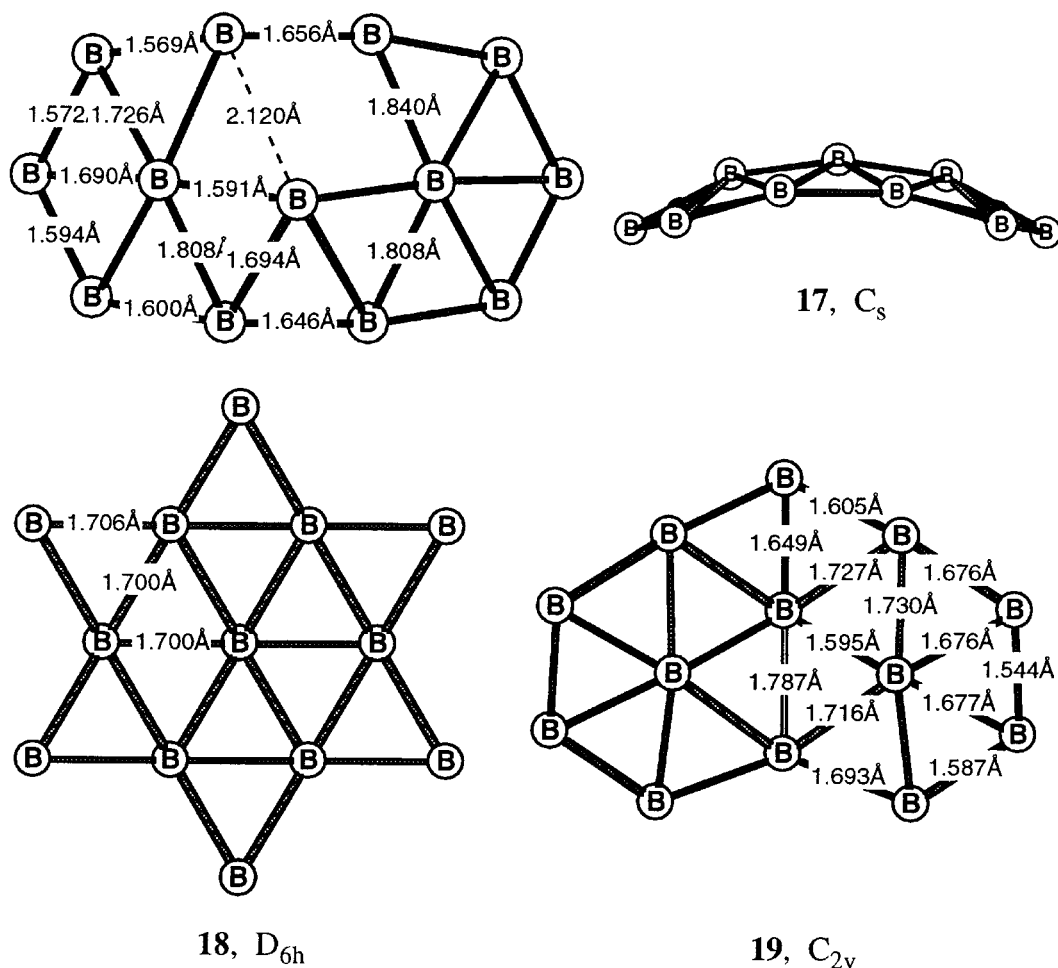


FIGURE 1. (Continued)

tures ($N_{\text{Imag}} = 1$), or higher order saddle points ($N_{\text{Imag}} > 1$).

Results and Discussions

B_{13}^+ CLUSTERS

Table I summarizes the computed total energies, the number of imaginary frequencies, the zero-point vibration energies (ZPVE), and the HOMO and LUMO energy separations as well as the relative energies for the B_{13}^+ clusters. The B3LYP/6-31G* optimized geometries are shown in Figure 1.

On the basis of its anomalously high experimental stability, Hanley et al.^{1b} suggested that B_{13}^+ should have an icosahedral structure with one encapsulated boron atom in the cluster center rather than capping a triangular face. Unfortun-

nately, this suggestion could not be confirmed computationally.^{6,7a} The D_{5d} B_{13}^+ cluster (1), distorted slightly from the I_h symmetrical structure, has seven imaginary frequencies (B3LYP/6-31G* level).

The planar C_{2v} B_{13}^+ structure (3), found to be an energy minimum at the HF/3-21G by Kato et al.,⁷ has two imaginary frequencies at the B3LYP/6-31G* level. Boustani's C_{2v} quasiplanar structure (4), a minimum at the LSD level of theory, but has one imaginary frequency at B3LYP/6-31G*.⁸ In contrast, the 3-dimensional C_{3v} structure (2) of Kawai and Weare⁶ and the planar C_{2v} structure (5) of Ricca and Bauschlicher⁹ are both energy minima. The latter is 44.6 kcal/mol lower in energy than the former.

In addition to 1-5, we optimized many other B_{13}^+ structures (6-19). Like the D_{5d} 1 form, none of the isomers containing one encapsulated boron

atom (6–9) are minima. In contrast to the C_{3v} Kawai structure (2),⁶ isomers 10 and 11 with one face coordinated boron atom are also higher order saddle points ($N_{\text{Imag}} \geq 1$). Neither the C_{2v} structure 12, an insertion product of one boron into the icosahedral B_{12} , nor the D_{2h} 13, which resembles two octahedra linked by one boron atom, are minima. In contrast to 6–13, we located two minima for 3-dimensional B_{13}^+ clusters derived from the D_{6d} B_{12} cluster. One is the D_{6d} 14 with one central encapsulated boron atom. The movement of the central boron atom in 14 out of the cage leads to the C_{6v} minimum 15 with one face coordinated boron atom, which is 0.76 eV lower in energy than 14.

Besides these 3-dimensional structures, we also explored some planar or quasiplanar B_{13}^+ isomers. For example, the D_{2h} 16, with three hexagons adjacent to one another in a linear arrangement, has two imaginary frequencies. Following the first vibration mode, the three six-coordinated boron atoms move slightly out of the plane; this results in the C_{2v} Boustani structure (4) with $N_{\text{Imag}} = 1$. Following the second vibration mode led to a C_s symmetrical minimum (17), only 1.0 kcal/mol lower in energy than 4 at B3LYP/6–31G*. The

planar structures 18 (D_{6h}) and 19 (C_{2v}) with $N_{\text{Imag}} > 1$ are higher order saddle points.

At the B3LYP/6–31G* level, the Ricca structure 5 (C_{2v}) has the lowest energy among all the B_{13}^+ isomers examined. The relative stability order for the minima (in kcal/mol) are 5 (0.0) > 17 (26.7) > 15 (44.5) \approx 2 (44.6) > 14 (62.0). However, the relative stability cannot be explained by the number of direct B–B connections (bonds). For example, 5 with 25 B–B bonds is the global minimum, whereas 14 is the highest energy isomer with 36 B–B connections. On the other hand, 15 and 2 with the same number of B–B bonds (30) are isoenergetic.

Furthermore, we have found a transition structure (5TS) at B3LYP/6–31G* for the degenerate rearrangement of 5. Both geometries are closely related. Indeed, when the ZPE (B3LYP/6–31G*) corrections are included, 5TS and 5 have essentially the same energies. Hence, the global minimum 5 should be highly fluxional.

In addition to the relative thermodynamic stability discussed above, the HOMO and LUMO energy separation ($\Delta\varepsilon$) should be related to the relative chemical reactivity¹⁴: the larger the $\Delta\varepsilon$, the less reactive the molecule. On this basis, the most thermodynamic stable 5 ($\Delta\varepsilon = 2.99$ eV) might

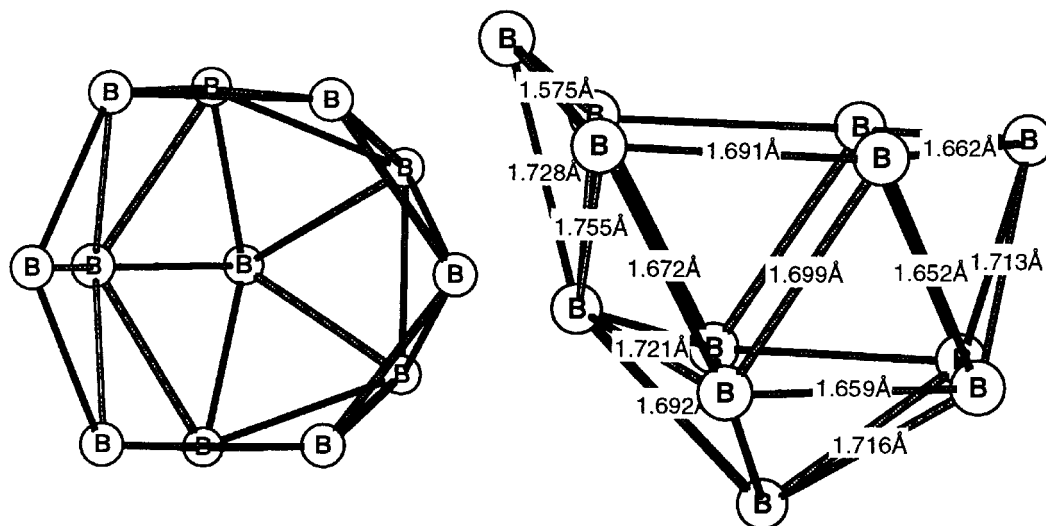
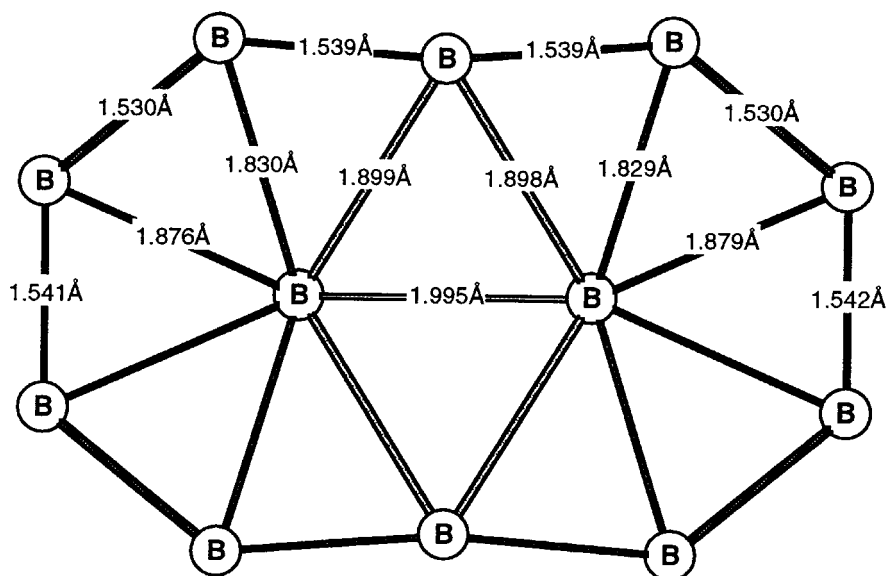
TABLE I.
Calculated Total Energies (E_{tot} , hartrees), Number of Imaginary Frequencies (N_{Imag}), Zero-Point Vibration Energies (ZPVE, kcal / mol), HOMO-LUMO Energy Separation ($\Delta\varepsilon$, eV), and Relative Energies (ΔH , kcal / mol) at B3LYP / 6–31G* Level for B_{13}^+ Clusters.

Systems	E_{tot} (N_{Imag})	ZPVE	$\Delta\varepsilon$	ΔH
1 (D_{5d} Anderson)	–322.14027 (7)	23.2	1.02	
2 (C_{3v} Kawai)	–322.47308 (0)	33.5	3.68	44.6
3 (C_{2v} Kato)	–322.33389 (2)	28.9	1.73	
4 (C_{2v} Boustani)	–322.50000 (1)	31.5	1.62	
5 (C_{2v} Ricca)	–322.54419 (0)	31.9	2.99	0.0
5TS (C_{2v})	–322.54378 (1)	31.7	–3.04	< 0.1
6 (D_{3d})	–322.09636 (7)	23.4	1.71	
7 (D_{2h})	–322.24490 (6)	26.0	1.85	
8 (C_{2v})	–322.42992 (1)	30.9	3.93	
9 (C_{2v})	–322.39226 (3)	28.6	2.51	
10 (C_{3v})	–322.30797 (6)	30.2	2.41	
11 (C_{4v})	–322.27292 (5)	29.0	2.50	
12 (C_{2v})	–322.40357 (1)	32.2	1.83	
13 (D_{2h})	–322.21701 (1)	30.5	1.71	
14 (D_{6d})	–322.44533 (0)	32.9	4.33	62.0
15 (C_{6v})	–322.47321 (0)	33.7	2.67	44.5
16 (D_{2h})	–322.49031 (2)	31.1	1.49	
17 (C_s)	–322.50160 (0)	32.1	1.91	26.7
18 (D_{6h})	–322.01669 (4)	22.1	0.89	
19 (C_{2v})	–322.42404 (2)	32.4	0.71	

TABLE II.

Calculated Total Energies (E_{tot} , hartrees), Number of Imaginary Frequencies (Nimag), Zero-Point Vibration Energies (ZPVE, kcal / mol), HOMO-LUMO Energy Separation ($\Delta\varepsilon$, eV), and Relative Energies (ΔH , kcal / mol) at B3LYP / 6-31G* Level for B_{12}^+ Clusters.

Systems	E_{tot} (Nimag)	ZPVE	$\Delta\varepsilon$	ΔH
20 (C_s Kawai)	-297.57341 (0)	31.1	2.05	57.8
21 (C_{2v})	-297.62915 (0)	27.2	1.73	18.9
22 (C_s)	-297.66283 (0)	29.4	1.51	0.0
23 (C_1 Ricca)	-297.66282 (0)	29.4	1.51	0.0
24 (C_1)	-297.61171 (0)	30.5	1.73	32.1

20, C_s (Kawai)21, C_{2v} FIGURE 2. Optimized structures of B_{12}^+ clusters at the B3LYP / 6-31G* level.

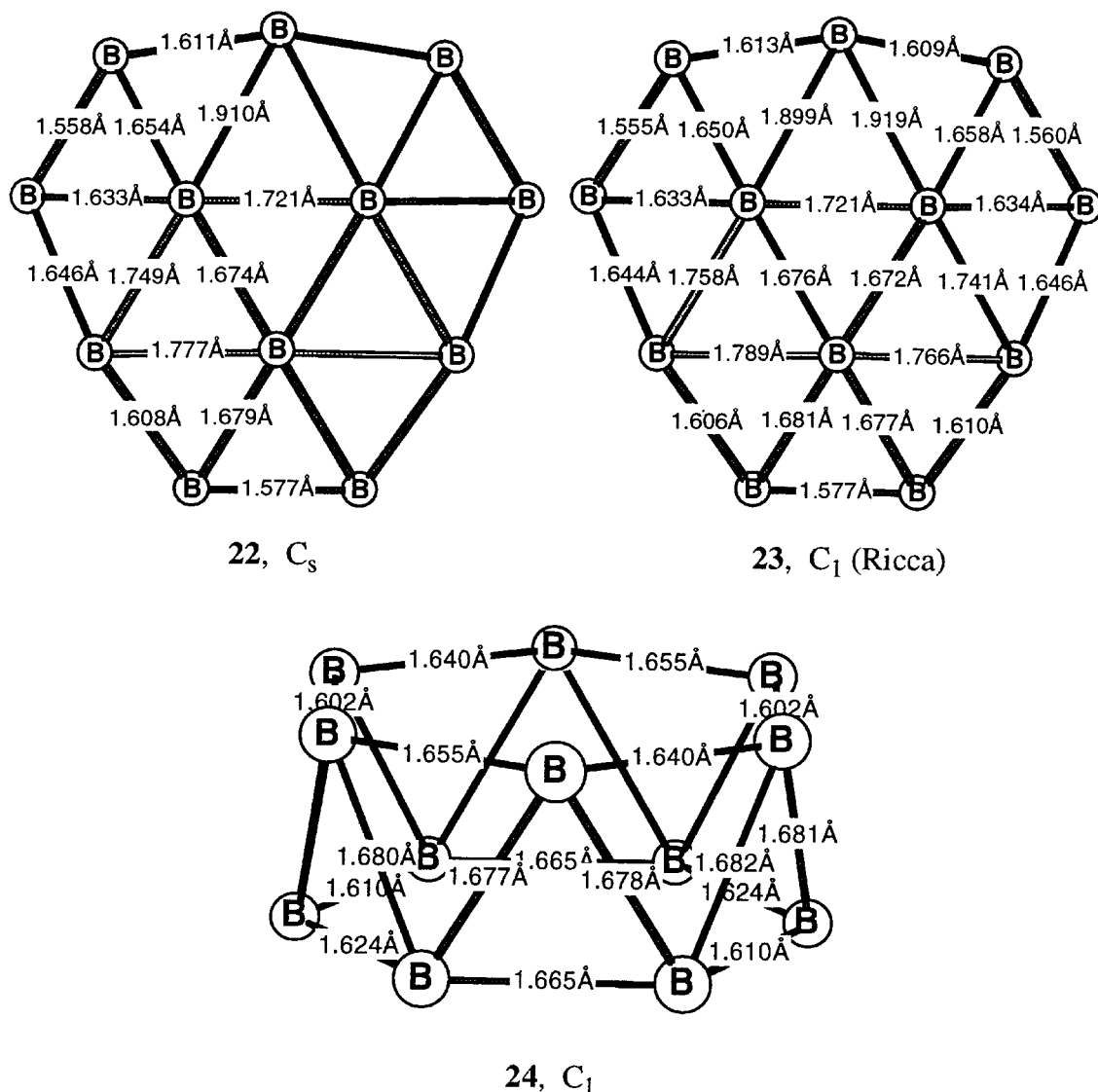


FIGURE 2. (Continued)

be more reactive than the 3-dimensional isomers ($\Delta\varepsilon = 3.68$ eV for **2** and $\Delta\varepsilon = 4.33$ eV for **14**).

B_{12}^+ CLUSTERS

Table II summarizes the computed total energies, the number of imaginary frequencies, the ZPVEs, and the energy separations between HOMO and LUMO as well as the relative energies of B_{12}^+ clusters. The B3LYP/6-31G* optimized geometries for all B_{12}^+ structures are shown in Figure 2. Here we concentrate mainly on the B_{12}^+ structures that are similar to their B_{13}^+ energy minimum counterparts.

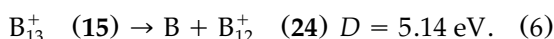
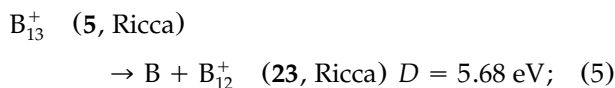
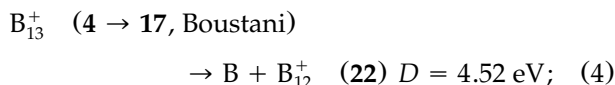
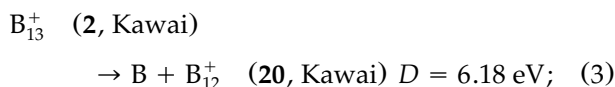
At B3LYP/6-31G*, the Kawai (C_{3v} , **20**)⁵ and the planar **21** (C_{2v}) structures are both minima. The starting point for **21** is based on the Kato HF/3-21G geometry.⁷ Due to the convergence problem in reproducing the Boustani C_{3v} structure (due to Jahn–Teller distortion), we altered the geometry slightly. This led to a C_s minimum (**22**) that had nearly the same energy as the C_1 Ricca and Bauschlicher structure (**23**) deduced from the Boustani C_{3v} structure (**8**). However, the difference in geometry between **22** and **23** is very significant (Fig. 2). Another 3-dimensional B_{12}^+ minimum (**24**, C_1) is derived from the C_{6v} B_{13}^+ **15**. As given in Table II, the most stable B_{12}^+ cluster isomers are **22**

and **23** that have quasiplanar structures. The planar Kato (**21**) and the two 3-dimensional (**20** and **24**) structures are high in energy.

Dissociation Energies of B_{13}^+ clusters

On the basis of the measured appearance potentials, Hanley et al.^{1a,b} found that the lowest energy dissociation process for B_{13}^+ involves the loss of a single neutral boron atom (B) and the formation of a B_{12}^+ cluster ($B_{13}^+ \rightarrow B + B_{12}^+$). Some energy minimum structures for B_{13}^+ have corresponding B_{12}^+ clusters with similar geometries (see Tables I, II). (Although the calculated relative energies reveal the thermodynamic stability, no information for the kinetic stability has been obtained.)

It can be questioned if only the global minimum is produced under the experimental conditions. What is the possibility for the coexistence of higher energy minimum structures? We can compare the dissociation process in various ways [eqs. (3)–(6)], first by assuming that the product has a structure (subunit) similar to that of the educt.



To estimate the dissociation energies for the B_n^+ clusters, Ricca and Bauschlicher⁹ calibrated the B3LYP/6–31G* results at the CCSD(T)/cc-pVTZ and found that B3LYP/6–31G* overestimates the dissociation energies by 0.5 eV on average. Using the same strategy we corrected the dissociation energies¹⁵ for the process in eqs. (3)–(6) by reducing the B3LYP/6–31G* values by 0.5 eV. As compared with the roughly estimated experimental result (8.0 ± 1.5 eV),^{1b} the Kawai structures (**2** and **20**) give the best agreement followed by the process leading from $B_{13}^+(\mathbf{5})$ to $B_{12}^+(\mathbf{23})$. Three-dimensional clusters give higher dissociation energies than the planar structures.

If we assume that all the possible interconversions of B_{13}^+ into B_{12}^+ can occur (i.e., that each stable B_{13}^+ clusters can dissociate into structurally

different B_{12}^+ clusters), the $B_{13}^+(\mathbf{5}) \rightarrow B_{12}^+(\mathbf{20})$ process has the largest dissociation energy (8.11 eV); this is very close to the experimental value (8.0 ± 1.5 eV).^{1b} Other processes such as $\mathbf{5} \rightarrow \mathbf{21}$, $\mathbf{5} \rightarrow \mathbf{24}$, and $\mathbf{17} \rightarrow \mathbf{20}$ give smaller values (6.6, 7.1, and 6.95 eV), but still within the experimental error limits.

Concluding Remarks

We confirmed (at B3LYP/6–31G*) that the most thermodynamically stable B_{12}^+ and B_{13}^+ clusters have planar or nearly planar structures; the 3-dimensional clusters were generally high in energy. However, the 3-dimensional energy minima (**2**, **14**) had larger HOMO-LUMO separations than the planar or quasiplanar structures. Hence, 3-dimensional structures may have lower chemical reactivity than their planar isomers. No direct relationship between the number of connections (bonds) and the relative stabilities was found. The calculated dissociation energies of 3-dimensional clusters were much closer to the large experimental range than the planar or quasiplanar structures. Therefore, planar and 3-dimensional structures of B_{13}^+ may both be formed experimentally. The reason for the high abundance of B_{13}^+ among the B_n^+ clusters is still an unsolved problem that challenges further experimental and theoretical investigations.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (NSFC) (Jilin, China), the Deutsche Forschungsgemeinschaft (DFG), and the Fonds der Chemischen Industrie (Erlangen, Germany). F. L. G. would like to thank Prof. Dr. P. Otto (Erlangen, Germany) for his encouragement and stimulating discussions.

References

- (a) L. Hanley and S. L. Anderson, *J. Phys. Chem.*, **91**, 5161 (1987); (b) L. Hanley, J. L. Whitten, and S. L. Anderson, *J. Phys. Chem.*, **92**, 5803 (1988); (c) L. Hanley and S. L. Anderson, *J. Chem. Phys.*, **89**, 2848 (1988); (d) S. A. Ruatta, L. Hanley, and S. L. Anderson, *J. Chem. Phys.*, **91**, 226 (1989); (e) P. A. Hintz, S. A. Ruatta, and S. L. Anderson, *J. Chem. Phys.*, **92**, 292 (1990); (f) S. A. Ruatta, P. A. Hintz, and S. L. Anderson, *J. Chem. Phys.*, **94**, 2833 (1991); (g) P. A. Hintz, M. B. Sowa, S. A. Ruatta, and S. L. Anderson, *J. Chem. Phys.*, **94**, 6446 (1991).

2. (a) P. A. Roland and J. J. Wynne, *J. Chem. Phys.*, **99**, 8599 (1993); (b) S. J. LaPlaca, P. A. Roland, and J. J. Wynne, *Chem. Phys. Lett.*, **190**, 163 (1992).
3. L. D. Brown and W. N. Lipscomb, *Inorg. Chem.*, **16**, 2989 (1977).
4. J. Donohue, *The Structures of the Elements*, Wiley, New York, 1974.
5. R. Kawai and J. H. Weare, *J. Chem. Phys.*, **95**, 1151 (1991).
6. R. Kawai and J. H. Weare, *Chem. Phys. Lett.*, **191**, 311 (1992).
7. (a) H. Kato, K. Yamashita, and K. Morokuma, *Bull. Chem. Soc. Jpn.*, **66**, 3358 (1993); (b) H. Kato, K. Yamashita, and K. Morokuma, *Chem. Phys. Lett.*, **190**, 361 (1992).
8. (a) I. Boustani, *Int. J. Quantum Chem.*, **52**, 1081 (1994); (b) I. Boustani, *Chem. Phys. Lett.*, **233**, 273 (1995); (c) I. Boustani, *Chem. Phys. Lett.*, **240**, 135 (1995); (d) I. Boustani, *Phys. Rev. B.*, **55**, 1 (1997); (e) I. Boustani, *Surf. Sci.*, **370**, 355 (1997); (f) I. Boustani, A. Quandt, and P. Kramer, *Europhys. Lett.*, **36**, 583 (1996).
9. A. Ricca and C. W. Bauschlicher, Jr., *Chem. Phys.*, **208**, 233 (1996).
10. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, *Gaussian 94, Revision C.3*, Gaussian, Inc., Pittsburgh, PA, 1995.
11. (a) W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986; (b) J. B. Foresman and A. E. Frisch, *Exploring Chemistry with Electronic Structure Methods: A Guide to Using Gaussian*, 2nd ed., Gaussian, Inc., Pittsburgh, PA, 1996.
12. (a) A. D. Becke, *Phys. Rev.*, **A38**, 3098 (1988); (b) A. D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993).
13. C. Lee, W. Yang, and R. G. Parr, *Phys. Rev.*, **B37**, 785 (1988).
14. (a) B. M. Trost, G. M. Bright, C. Frihart, and D. Brittelli, *J. Am. Chem. Soc.*, **93**, 737 (1971); (b) C. F. Wilcox, Jr., J. P. Uetrecht, G. D. Grantham, and K. G. Grohmann, *J. Am. Chem. Soc.*, **97**, 1914 (1977); (c) K. N. Houk, *Acc. Chem. Res.*, **8**, 361 (1975); (d) R. C. Haddon and T. Fukunaga, *Tetrahedron Lett.*, **21**, 1191 (1980).
15. The B3LYP/6-31G* energy for the B atom is -24.65435 au.